

0 **System and Method for Production of Optically Transparent and Electrically Conductive
Coatings**

Patent Application of

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5 The present invention results from a research sponsored by the SBIR Program of the U.S.
National Science Foundation. The U.S. government has certain rights on this invention.

FIELD OF THE INVENTION

10 The present invention relates to a method and associated system for producing an
optically transparent and electrically conductive coating on a substrate that is most suitable for
use in liquid crystal displays (LCD), electrodes in solar batteries, anti-static shields, or
electromagnetic wave shields, etc.

BACKGROUND OF THE INVENTION

15 Transparent, electro-conductive substrates are obtained by two primary methods. The
first method entails producing a thin film of an oxide, such as indium-tin oxide (hereinafter
referred to as "ITO") or antimony-tin oxide ("ATO"), on a transparent glass or plastic substrate
by sputtering or chemical vapor deposition (CVD). The second method involves coating a
transparent, electro-conductive ink on a support such as a glass substrate. The ink composition
contains a powder of ultra-fine, electro-conductive particles having a particle size smaller than
the smallest wavelength of visible rays. The ink is then dried on the support, which is then baked
at temperatures of 400°C or higher.

20 The first method requires the utilization of expensive devices and its reproducibility and
yield are low. Furthermore, the procedure is tedious and time-consuming, typically involving the
preparation of fine oxide particles, compaction and sintering of these fine particles to form a
target, and then sputtering of this target in a high-vacuum environment. Therefore, it was

0 difficult to obtain low-priced, transparent, electro-conductive coatings. The electro-conductive
film formed on the support by the second method tends to have some gaps remaining between
the ultra-fine particles thereon so that light scatters on the film, resulting in poor optical
properties. In order to fill the gaps, heretofore, a process has been proposed in which a
glass-forming component is incorporated into the transparent, electro-conductive ink prior to
5 forming the transparent, electro-conductive substrate. However, the glass-forming component is
problematic in that it exists between the ultra-fine, electro-conductive particles, thereby
increasing the surface resistivity of the electro-conductive film to be formed on the support. For
this reason, therefore, it was difficult to satisfy both the optical characteristics and the desired
surface resistivity conditions of the transparent, electro-conductive substrate by the
10 above-mentioned second method. In addition, the transparent, electro-conductive substrate
formed by the second method has exhibited poor weatherability. When the substrate is allowed
to stand in air, the resistance of the film coated thereon tends to increase with time.

15 The present invention has been made in consideration of these problems in the related
prior arts, and its object is to provide a cost-effective method for directly forming a transparent,
electro-conductive coating onto a glass or plastic substrate. In order to produce a uniform, thin,
and optically transparent oxide coating on a glass substrate, it is essential to produce depositable
oxide species that are in the vapor state prior to striking the substrate. These oxide species are
preferably individual oxide molecules or nanometer-sized clusters.

20 In one embodiment of the present invention, a method entails producing ultra-fine vapor
clusters of oxide species and directing these clusters to impinge upon a substrate, permitting
these clusters to become solidified thereon to form a thin coating layer. These nano clusters are
produced by operating a twin-wire arc nozzle in a chamber to produce metal clusters and by
introducing an oxygen-containing gas into the chamber to react with the metal clusters, thereby
converting these metal clusters into nanometer-sized oxide clusters. The heat generated by the
25 exothermic oxidation reaction can in turn accelerate the oxidation process and, therefore, make
the process self-sustaining or self-propagating. The great amount of heat released can also help
to maintain the resulting oxide clusters in the vapor state. Rather than cooling and collecting

0 these clusters to form individual powder particles, these nanometer-sized vapor clusters can be directed to form an ultra-thin oxide coating onto a glass or plastic substrate. Selected oxide coatings such as, zinc oxide, ITO and ATO, are optically transparent and electrically conductive.

SUMMARY OF THE INVENTION

5 A preferred embodiment of the present invention is a method for producing an optically transparent and electrically conductive coating onto a substrate. The method includes three primary steps: (a) operating a twin-wire arc nozzle to provide a stream of nano-sized metal vapor clusters into a coating chamber in which the substrate is disposed; (b) introducing a stream of oxygen-containing gas into this chamber to impinge upon the stream of metal vapor clusters and exothermically react therewith to produce substantially nanometer-sized metal oxide clusters; and (c) directing these metal oxide clusters to deposit onto the substrate for forming the desired coating.

10 In the first step, the method begins with feeding a pair of metal wires (either a pure metal or metal alloy) into the upper portion of a coating chamber. The respective leading tips of the two wires are first brought to be in physical contact with each other to form a tentative "short circuit" under a high-current condition and, with the presence of a working gas, form an ionized arc. The arc will heat and vaporize the tips to form nano-sized metal clusters. While the wire tips are being consumed by the arc, the wires are continuously or intermittently fed into an arc cell so that the two leading tips are maintained at a relatively constant separation in a working gas environment. An oxygen-containing gas is introduced into the chamber to react with the metal vapor clusters to form metal oxide clusters. In this case, the oxygen-containing gas serves to provide the needed oxygen for initiating and propagating the exothermic oxidation reaction to form the oxide clusters in the liquid or vapor state, which are then deposited onto the substrate to form a thin coating.

25 The twin-wire arc spray process, originally designed for the purpose of thermal spray coating, can be adapted for providing a continuous stream of metal vapor clusters. This is a low-cost process that is capable of readily heating up the metal wire to a temperature as high as

0 6,000°C. In an electric arc, the metal is rapidly heated to an ultra-high temperature and is vaporized essentially instantaneously. Since the wires can be continuously fed into the arc-forming cell, the arc vaporization is a continuous process, which means a high coating rate.

5 The presently invented method is applicable to essentially all metallic materials, including pure metals and metal alloys. When high service temperatures are not required, the metal may be selected from the low melting point group consisting of antimony, bismuth, cadmium, cesium, gallium, indium, lead, lithium, rubidium, selenium, tin, and zinc. When a high service temperature is required, a metallic element may be selected from the high-melting refractory group consisting of tungsten, molybdenum, tantalum, hafnium and niobium. Other metals with intermediate melting points such as copper, zinc, aluminum, iron, nickel and cobalt may also be selected. Indium, tin, zinc, and antimony are currently the preferred choices of metal for practicing the present invention for liquid crystal display applications.

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Preferably the reactive gas is an oxygen-containing gas, which includes oxygen and, optionally, a predetermined amount of a second gas selected from the group consisting of argon, helium, hydrogen, carbon, nitrogen, chlorine, fluorine, boron, sulfur, phosphorus, selenium, tellurium, arsenic and combinations thereof. Argon and helium are noble gases and can be used as a carrier gas (without involving any chemical reaction) or as a means to regulate the oxidation rate. Other gases may be used to react with the metal clusters to form compound or ceramic phases of hydride, oxide, carbide, nitride, chloride, fluoride, boride, sulfide, phosphide, selenide, telluride, and arsenide in the resulting coating if so desired.

20 Specifically, if the reactive gas contains oxygen, this reactive gas will rapidly react with the metal clusters to form nanometer-sized ceramic clusters (e.g., oxides). If the reactive gas contains a mixture of two or more reactive gases (e.g., oxygen and nitrogen), the resulting product will contain a mixture of oxide and nitride clusters. If the metal composition is a metal alloy or mixture (e.g., containing both indium and tin elements) and the reactive gas is oxygen, the resulting product will contain ultra-fine indium-tin oxide clusters that can be directed to deposit onto a glass or plastic substrate.

0 At a high arc temperature, metal clusters are normally capable of initiating a substantially spontaneous reaction with a reactant species (e.g., oxygen). In this case, the reaction heat released is effectively used to sustain the reactions in an already high temperature environment.

5 Still another preferred embodiment is a system for producing an optically transparent, electrically conductive coating onto a substrate. The system includes:

- (a) a coating chamber to accommodate the substrate,
- (b) a twin-wire electrode device in supplying relation to the coating chamber for supplying nano-scaled clusters of a metal composition therein. The electrode device includes: (i) two wires made up of this metal composition, with each wire having a leading tip which is continuously or
- 10 intermittently fed into the coating chamber in such a fashion that the two leading tips are maintained at a desired separation; and (ii) means for providing electric currents and a working gas flow for creating an ionized arc between the two leading tips for melting and vaporizing the metal composition to generate the nano-scaled metal clusters;
- (c) gas supply means disposed a distance from the chamber for supplying a reactive gas into the
- 15 chamber to react with the nano-scaled clusters therein for forming substantially nanometer-sized metal compound or ceramic clusters; and
- (d) supporting-conveying means to support and position the substrate into the chamber, permitting the metal compound or ceramic clusters to deposit and form a coating onto the substrate. Preferably, the supporting-conveying means are made to be capable of transferring, intermittently or continuously, a train of substrate glass pieces into the deposition chamber for
- 20 receiving the depositable oxide clusters and then transferring them out of the chamber once a coating of a desired thickness is deposited on the substrate.

Advantages of the present invention are summarized as follows:

1. A wide variety of metallic elements can be readily converted into nanometer-scaled oxide
- 25 clusters for deposition onto a glass or plastic substrate. The starting metal materials can be selected from any element in the periodic table that is considered to be metallic. In addition to oxygen, partner gas species may be selected from the group consisting of hydrogen, carbon, nitrogen, chlorine, fluorine, boron, sulfur, phosphorus, selenium,

0 tellurium, arsenic and combinations thereof to help regulate the oxidation rate and, if so
desired, form respectively metal hydrides, oxides, carbides, nitrides, chlorides, fluorides,
borides, sulfides, phosphide, selenide, telluride, arsenide and combinations thereof. No
known prior-art technique is so versatile in terms of readily producing so many different
types of ceramic coatings on a substrate.

- 5 2. The metal composition can be an alloy of two or more elements which are uniformly
dispersed. When broken up into nano-sized clusters, these elements remain uniformly
dispersed and are capable of reacting with oxygen to form uniformly mixed ceramic
coating, such as indium-tin oxide. No post-fabrication mixing treatment is necessary.
- 10 3. The twin wires can be fed into the arc cell at a high rate with their leading tips readily
vaporized. This feature makes the method fast and effective and now makes it possible to
mass produce transparent and conductive coatings on a substrate cost-effectively.
- 15 4. The system needed to carry out the invented method is simple and easy to operate. It does
not require the utilization of heavy and expensive equipment such as a laser or vacuum-
sputtering unit. In contrast, it is difficult for a method that involves a high vacuum to be a
continuous process. The over-all product costs produced by the presently invented
vacuum-free method are very low.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 shows the schematic of a preferred embodiment of a system for producing oxide coating
on a substrate.

FIG.2 schematically shows the working principle of an electric arc spray-based device for
generating a stream of nano-sized metal vapor clusters: (a) an open-style arc-spray nozzle
and (b) a closed-style arc-spray nozzle in which the arc zone is enclosed by an air cap 76.

FIG.3 the twin-wire arc nozzle further equipped with a plasma arc device for generating a
plasma arc zone downstream from the twin-wire arc..

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Figure 1 schematically shows a coating system, in accordance with a preferred
embodiment of the present invention, for producing an optically clear and electrically conductive

0 coating on a glass or plastic substrate. This apparatus includes four major functional components: (1) a coating chamber 90, (2) a twin-wire arc nozzle means 10, (3) reactive gas-supplier (e.g., a gas bottle 53 supplying a reactive gas through a valve 57 and pipe means 59 into a location inside the chamber downstream from the ionized arc 66), and (4) substrate supporter-conveyor (e.g., conveying rollers 92a,92b,92c,92d and belt 96).

5 In a preferred embodiment of the presently invented system, as indicated in FIG.1, the twin-wire electric arc spray nozzle is mainly composed of an electrically insulating block 74, two feed wires 50, 52, a working gas passage means 60, and a secondary gas nozzle with a gas passage 78. The two metal wires 50,52 are supplied with a DC voltage (one "+" and the other "-") or a pulsed power 70 to form an arc 66 in an arc chamber 51. This arc 66, being at an ultra-
10 high temperature (up to 6,000°C), functions to melt and vaporize the wire tips to generate nano-sized metal vapor clusters. A stream of working/carrier gas from a source 62 (not shown; denoted by an arrow) passes through the passage means 60 into the arc chamber 51 to help maintain the ionized arc and to carry the stream of metal vapor clusters downward toward lower portion of the coating chamber 90.

15 The two wires 50,52 can be fed through air-tight means 55a,55b into the arc cell 51, continuously or intermittently on demand, by a wire-feeding device (e.g., powered rollers 54). The roller speed may be varied by changing the speed of a controlling motor. An optional secondary gas nozzle (having a gas passage 78) can be used to further increase the arc temperature, providing a stream of super-heated ultra-fine metal vapor clusters into the coating
20 chamber 90.

A reactive gas such as an oxygen-containing gas provided from a gas cylinder 53 goes through a gas regulator or control valve 57 and tubing 59 into a location 82 downstream from the ionized arc 66 inside the coating chamber. The gas regulator or control valve 57 is used to adjust the gas flow rate as a way to vary the effective coating rate. The oxygen gas impinges upon the
25 metal clusters to initiate and sustain an exothermic oxidation reaction between oxygen and metal clusters, thereby converting the ultra-fine metal clusters into depositable metal oxide clusters 85

that are in the liquid or, preferably, vapor state.

The ultra-fine oxide clusters **85** are then directed to deposit onto a glass or plastic substrate (e.g., **94b**) being supported by a conveyor belt **96** which is driven by 4 conveyor rollers **92a-92d**. The lower portion of FIG.1 shows a train of substrate glass pieces, including **94a** (uncoated), **94b** (being coated) and **94c** (coated). The oxide clusters that are not deposited will be cooled to solidify and become solid powder particles. These powder particles, along with the residual working gas and carrier gas, are transferred through a conduit to an optional powder collector/separator system (not shown).

The twin-wire arc spray nozzle, originally developed for use in a conventional thermal spray coating process, can be adapted for providing a continuous stream of super-heated metal vapor clusters. This low-cost device, capable of readily heating up the metal wire to a temperature as high as 6,000°C, is further illustrated in FIG.2a and 2b.

Schematically shown in FIG.2a is an open-style twin-wire arc spray nozzle. Two metal wires **50,52** are driven by powered rollers **54** to come in physical contact with two respective conductive jackets **72** which are supplied with “+” and “-” voltage or pulsed power through electrically conductive blocks **56** and **58**, respectively. The voltage polarity may be reversed; i.e., “-” and “+” instead of “+” and “-”. The voltages may come from either a DC or a pulsed power source **70**. The lower ends of the two wires approach each other at an angle of approximately 30-60°. The two ends are brought to contact each other for a very brief period of time. Such a “short circuit” contact creates an ultra-high temperature due to a high current density, leading to the formation of an arc **66**. A stable arc can be maintained provided that the voltage is constantly supplied, a certain level of gas pressure is maintained, and the wires are fed at a constant or pulsating speed. A stream **64** of compressed air, introduced through a gas passage **60** from a gas source (e.g., compressed air bottle, not shown), serves to provide such a working gas, which also helps to carry the metal clusters downward toward the substrate. The system may further include means for providing dissociable inert gas mixable with the working gas, the dissociable inert gas increasing the temperature gradient in the ionized arc.

0 A closed-style arc spray nozzle is schematically shown in FIG.2b. In this spray arc
nozzle, the arc zone is enclosed by an air cap 76 in a block 74 and additional compressed gas or
air (referred to as the secondary gas) is introduced (e.g., from 78) into the arc zone to compress
the arc. The increased arc zone pressure effectively increases the arc temperature, thereby
promoting the more efficient metal vaporization and finer metal vapor clusters. These super-
5 heated fine vapor clusters (e.g., 68) are then carried into the coating chamber for reaction with
oxygen to form oxide clusters.

Twin-arc spray nozzles have been advanced to the extent that they provide reliable and
stable ultra-high temperature arcs. These low cost devices are available from several commercial
sources. Examples of these devices can be found in the following patents: U.S. Pat. No.
10 4,095,081 (June 13, 1978 to S. J. Ashman), No.4,668,852 (May 26, 1987 to T. J. Fox, et al.), and
No.5,964,405 (Oct.12, 1999 to R. Benary, et al.).

In another embodiment of the invented system, the two wires are made up of two
different materials so that a mixture of two types of nano clusters can be produced for the
purpose of depositing a hybrid or composite coating material.

15 In a preferred embodiment, the system (for both cases of two wires of the same material
and of different materials) as defined above may further include a second plasma arc zone below
the ionized arc between the two wire tips to vaporize any un-vaporized material dripped
therefrom. For instance, a plasma arc device (e.g., with electrodes 67 in FIG.3) may be utilized
to generate a plasma arc zone 69 through which the un-vaporized melt droplets dripped out of the
20 ionized arc 66 will have another chance to get vaporized. The creation of a plasma arc zone is
well-known in the art. The ultra-high temperature in the plasma arc (up to as high as 32,000°K)
rapidly vaporizes the melt droplets that pass through the plasma arc zone.

For the purpose of clearly defining the claims, the word "wire" means a wire of any
practical diameter, e.g., from several microns (a thin wire or fiber) to several centimeters (a long,
25 thick rod). A wire can be supplied from a spool, which could provide an uninterrupted supply of

0 a wire as long as several miles. This is a very advantageous feature, since it makes the related coating process a continuous one.

The presently invented system is applicable to essentially all metallic materials (including pure metals and metal alloys), metal compounds, and ceramic materials. As used herein, the term "metal" refers to an element of Groups 2 through 13, inclusive, plus selected elements in Groups 14 and 15 of the periodic table. Thus, the term "metal" broadly refers to the following elements:

- Group 2 or IIA: beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra).
- Groups 3-12: transition metals (Groups IIIB, IVB, VB, VIB, VIIB, VIII, IB, and IIB), including scandium (Sc), yttrium (Y), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo), tungsten (W), manganese (Mn), technetium (Tc), rhenium (Re), iron (Fe), ruthenium (Ru), osmium (Os), cobalt (Co), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd), platinum (Pt), copper (Cu), silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and mercury (Hg).
- Group 13 or IIIA: boron (B), aluminum (Al), gallium (Ga), indium (In), and thallium (Tl).
- Lanthanides: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).
- Group 14 or IVA: germanium (Ge), tin (Sn), and lead (Pb).
- Group 15 or VA: antimony (Sb) and bismuth (Bi).

When high service temperatures are not required, the component metal element may be selected from the low melting point group consisting of bismuth, cadmium, cesium, gallium, indium, lead, lithium, rubidium, tin, and zinc, etc. When a high service temperature is required, a metallic element may be selected from the high-melting refractory group consisting of tungsten,

0 molybdenum, tantalum, hafnium and niobium. Other metals with intermediate melting points such as copper, zinc, aluminum, iron, nickel and cobalt may also be selected. However, for the purpose of producing optically transparent and electrically conductive coating, indium, tin, antimony, and zinc are the most preferred metallic elements.

5 Preferably the reactive gas includes a gas selected from the group consisting of hydrogen, oxygen, carbon, nitrogen, chlorine, fluorine, boron, iodine, sulfur, phosphorus, arsenic, selenium, tellurium and combinations thereof. Noble gases such as argon and helium may be used to adjust or regulate the oxidation rate. Other gases may be used to react with the metal clusters to form nanometer-scale compound or ceramic powders of hydride, oxide, carbide, nitride, chloride, fluoride, boride, iodide, sulfide, phosphide, arsenide, selenide, and telluride, and combinations thereof.

10 If the reactive gas contains a reactive gas (e.g., oxygen), this reactive gas will rapidly react with the metal clusters to form nanometer-sized ceramic clusters (e.g., oxides). If the reactive gas contains a mixture of two or more reactive gases (e.g., oxygen and nitrogen), the resulting product will contain a mixture of two compounds or ceramics (e.g., oxide and nitride).
15 If the metal wire is a metal alloy or mixture (e.g., containing both indium and tin elements) and the reactive gas is oxygen, the resulting product will contain ultra-fine indium-tin oxide particles.

Another embodiment of the present invention is a method for producing an optically transparent and electrically conductive coating onto a transparent substrate. The method includes three steps:

- 20 (a) operating a twin-wire arc nozzle to heat and at least partially vaporize two wires of a metal composition for providing a stream of nanometer-sized metal vapor clusters into a chamber in which the substrate to be coated is disposed;
- (b) introducing a stream of oxygen-containing gas into this chamber to impinge upon this stream of metal vapor clusters and exothermically react therewith to produce substantially
25 nanometer-sized metal oxide clusters (in liquid or vapor state, preferably vapor state); and
- (c) directing the metal oxide clusters to deposit onto the substrate for forming the coating.

0 Optionally, the method may include another step of operating a plasma arc means for vaporizing any un-vaporized metal after step (a) and before step (b). Also optionally, the method may include an additional step of operating a plasma arc means for vaporizing any un-vaporized metal oxide clusters after step (b) and before step (c).

5 In the presently invented method, the stream of reactive gas or oxygen-containing gas may further include a small amount of a second gas to produce a small proportion of compound or ceramic clusters that could serve to modify the properties of the otherwise pure oxide coating. This second gas may be selected from the group consisting of hydrogen, carbon, nitrogen, chlorine, fluorine, boron, sulfur, phosphorus, arsenic, selenium, tellurium and combinations thereof.

10 Preferably, the transparent substrate in the practice of the present method includes a train of individual pieces of glass or plastic being moved sequentially or concurrently into coating chamber and then moved out of the chamber after the coating is formed. This feature will make the process a continuous one.

15 In another embodiment of the method, the metal composition may include an alloy or mixture of at least two metallic elements, with a primary one occupying more than 95% and the minor one less than 5% by atomic number. The primary one is selected so that its metal vapor clusters can be readily converted to become oxides or other ceramic clusters. However, the minor one may be allowed to remain essentially as nano-sized metal clusters. Upon deposition onto the substrate, the minor metal element only serves as a modifier to the properties (e.g., to increase the electrical conductivity) of the oxide coating. The presence of a small amount of nano-scaled metal domains does not adversely affect the optical transparency of the oxide coating.

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 In the presently invented method, the stream of oxygen-containing gas reacts with the metal vapor clusters in such a manner that the reaction heat released is used to sustain the

